

PATENT ABSTRACTS OF JAPAN

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(71)Applicant : SANYO ELECTRIC CO LTD

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(72)Inventor : MITA HIROKO

NAKANE IKURO

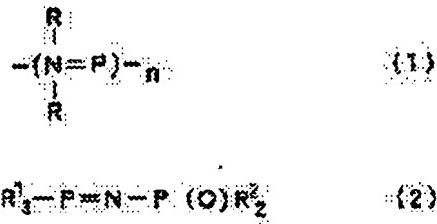
UBUKAWA SATOSHI

(54) NONAQUEOUS ELECTROLYTE BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a nonaqueous electrolyte battery superior in discharge property at an initial state and after high-temperature storage and hard to fire and highly safe even in the case of the destruction of an exterior can.

SOLUTION: A phosphagen compound and an amide compound are added to an electrolyte of a nonaqueous electrolyte battery having a positive electrode and a negative electrode. Preferably as the phosphazene compound, both a cyclic phosphazene compound represented by a general formula (1), where n=3-5, R is a halogen element, a halogen substituent group, a alkyl group or aromatic, and a chain phosphazene compound represented by a general formula (2), where R₁ is a halogen substituent group and R₂ is an alkyl group or a halogen substituent group.



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CLAIMS

[Claim(s)]

[Claim 1] The nonaqueous electrolyte cell by which the separator inserted between the positive electrode, the negative electrode, and said positive electrode and negative electrode and nonaqueous electrolyte were provided, and the phosphazene compound and the amide compound were added by said nonaqueous electrolyte.

[Claim 2] The nonaqueous electrolyte cell according to claim 1 by which said phosphazene compound contains an annular phosphazene compound and a chain-like phosphazene compound.

[Claim 3] The nonaqueous electrolyte cell according to claim 2 by which said annular phosphazene compound contains the matter expressed with the following formulas (1).

[Formula 1]



ただし、 $n = 3 \sim 5$

Rは、ハロゲン元素、ハロゲン置換基、アルキル基、または芳香族

[Claim 4] The nonaqueous electrolyte cell according to claim 2 by which said chain-like phosphazene compound contains the matter expressed with the following formulas (2).

[Formula 2]



ただし、 R^1 は、ハロゲン置換基

R^2 は、アルキル基またはハロゲン置換基

[Claim 5] The nonaqueous electrolyte cell according to claim 2 which contains said annular phosphazene compound and a chain-like phosphazene compound 40/60-80/20 with the mass ratio of an annular phosphazene compound / chain-like phosphazene compound.

[Claim 6] The nonaqueous electrolyte cell according to claim 1 by which 0.05-90 mass % addition of said phosphazene compound was done to said nonaqueous electrolyte.

[Claim 7] The nonaqueous electrolyte cell according to claim 1 by which 0.5-50 mass % addition of said phosphazene compound was done to said nonaqueous electrolyte.

[Claim 8] The nonaqueous electrolyte cell according to claim 1 by which 1-20 mass % addition of said phosphazene compound was done to said nonaqueous electrolyte.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the amelioration for raising the elevated-temperature preservation property and safety in more detail about the nonaqueous electrolyte cell which uses a lithium as an active material.

[0002]

[Description of the Prior Art] With the request of the miniaturization of a pocket device in recent years, or high-performance-izing, a miniaturization and high-performance-izing of the cell division rechargeable battery as those driving sources are called for. The nonaqueous electrolyte cell which used the lithium for the active material attracts attention widely from energy density being high.

[0003] If the nonaqueous electrolyte cell of a charge condition is saved at an elevated temperature 60 degrees C or more, since the so-called passive state film is formed in an active material front face, the internal resistance of a cell will rise and discharge capacity will fall greatly. Furthermore, the nonaqueous electrolyte cell has been the problem that the fire-resistant improvement at the time of an electrolyte beginning to leak is big from a viewpoint of the safety at the time of the use.

[0004] For improvement in an elevated-temperature preservation property and fire retardancy, the phosphazene compound to an electrolyte or addition of phosphoric ester is considered widely. Since the film which reacts with the ingredient which constitutes a positive electrode or a negative electrode, and consists of the resultant is formed in an electrode surface, the electrolyte which added the phosphoric ester compound is one side of improvement in fire retardancy, and brings about aggravation of a cycle property, and the rise of internal impedance. Moreover, the effectiveness over fire-resistant improvement is also small. The nonaqueous electrolyte cell which added a phosphazene compound and phosphoric ester to the electrolyte is proposed by JP,11-191431,A there. The coat by which phosphazene was stabilized was formed in the electrode surface by adding a phosphazene compound to an electrolyte at phosphoric ester and coincidence, and the formation and growth of a coat resulting from addition of a phosphoric ester compound are controlled. However, by this proposal, the fall of the discharge property of a cell cannot fully be controlled under the effect of the phosphazene film formed in an active material front face.

[0005] So, the nonaqueous electrolyte cell containing a phosphazene compound or radical polymerization inhibitor is proposed by JP,2001-23687,A. However, it is difficult to secure an elevated-temperature preservation property and fire retardancy on high level also by this proposal.

[0006]

[Problem(s) to be Solved by the Invention] It is for solving the above-mentioned trouble, this invention is excellent in the discharge property after first stage and elevated-temperature preservation, and also when a sheathing can is destroyed further, it aims at offering a nonaqueous electrolyte cell with the high safety which ignition cannot produce easily.

[0007]

[Means for Solving the Problem] In this invention, a phosphazene compound and an amide compound are added in an electrolyte. While a phosphazene compound and an amide compound do not check electrode reaction under an ordinary temperature environment, they form the coat which reacts to the bottom of hot environments mutually, and controls electrode reaction on an active material front face. Here, it is guessed that the film formed is that in which a phosphazene compound incorporates the nitrogen of an amide compound,

carries out a polymerization, and is formed. Therefore, an elevated-temperature preservation property can be raised, without usually reducing the property at the time of use. Moreover, it contributes also to the fire-resistant improvement in an electrolyte. That is, the preservation property of a cell and fire retardancy improve according to a mutual operation with a phosphazene compound and an amide compound.

[0008]

[Embodiment of the Invention] The nonaqueous electrolyte cell of this invention is equipped with the separator inserted between the positive electrode, the negative electrode, the positive electrode, and the negative electrode, and nonaqueous electrolyte, and the phosphazene compound and the amide compound are further added by nonaqueous electrolyte. As a phosphazene compound, it is desirable to include the both sides of an annular phosphazene compound and a chain-like phosphazene compound. Addition of an annular phosphazene compound is useful to fire-resistant improvement. Since a chain-like phosphazene compound is excellent in the solubility over an electrolyte, it can make electrolytic phosphazene concentration high by using it. The annular phosphazene compound used by this invention is preferably expressed with the following formulas (1).

[0009]

[Formula 3]



ただし、n = 3 ~ 5

Rは、ハロゲン元素、ハロゲン置換基、アルキル基、または芳香族

[0010] Moreover, a chain-like phosphazene compound is expressed with the following formulas (2).

[0011]

[Formula 4]



[0012] Here, R1 contains the halogenation radical of OCH₂CF₃, OCH₂CF₂CF₃, and OCF₂CF₂CH₃ grade. R2 contains the alkyl group and halogenation radical of for example, CH₂CH₃ grade.

[0013] Fire retardancy can be raised without worsening the property of further others, if chain-like phosphazene and annular phosphazene are included by the moderate ratio. If an annular phosphazene compound and a chain-like phosphazene compound are added with the mass ratio of (an annular phosphazene compound / chain-like phosphazene compound) so that it may be set to 40 / 60 - 80/20, the nonaqueous electrolyte cell excellent in an elevated-temperature preservation property and fire-resistant both sides will be obtained. To an electrolyte, even if it is addition of the minute amount of 0.05 mass % extent, big effectiveness is acquired in an elevated-temperature preservation property and fire retardancy. If the addition of a phosphazene compound exceeds 90 mass %, initial discharge capacity will be affected. the addition of a phosphazene compound -- desirable -- an electrolyte -- receiving -- 0.5 to 50 mass % -- it is one to 20 mass % more preferably. An amide compound is made desirable 0.5-5 mass % addition to an electrolyte. A phosphazene compound and an amide compound react to the bottom of hot environments, do not form a coat in an active material front face, and do not check electrode reaction under an ordinary temperature environment. Therefore, an elevated-temperature preservation property can be raised, without usually reducing the property at the time of use.

[0014] LiCoO₂, LiNiO₂, LiMn₂O₄, MnO(s)₂, and such mixture are used for a positive electrode. For example, a lithium metal or a lithium alloy is used for a negative electrode. Moreover, carbon materials, such as a graphite and corks, and the alloys containing Si or Sn and those oxides can also be used.

[0015]

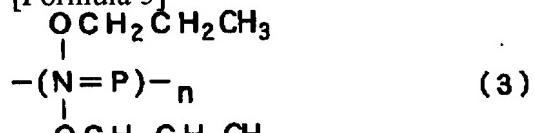
[Example] The fire retardancy of the electrolyte containing a phosphazene compound and an amide compound was actually evaluated, further, the cell was assembled using them and the initial discharge property and an elevated-temperature preservation property were evaluated.

[0016] After mixing ethylene carbonate and diethylene carbonate by the volume ratio of 3:7, it dissolved so that it might become this in 1. and one mol /to this mixed solvent about LiPF₆, and nonaqueous electrolyte was obtained. The specified quantity dissolution of the N methyl acetamide was carried out as the annular

phosphazene compound shown in the obtained nonaqueous electrolyte by the following formulas (3), the chain-like phosphazene compound shown by the formula (4), and an amide compound.

[0017]

[Formula 5]



ただし、n=3

[0018]

[Formula 6]



[0019] 1 mass % addition of N methyl acetamide was done to nonaqueous electrolyte at nonaqueous electrolyte, and 20 mass % addition of an annular phosphazene compound was further done to nonaqueous electrolyte at this. This is made into an example 1. 1 mass % addition of N methyl acetamide was done to nonaqueous electrolyte at nonaqueous electrolyte, and 20 mass % addition of a chain-like phosphazene compound was further done to nonaqueous electrolyte at this. This is made into an example 2. 1 mass % addition of N methyl acetamide was done to nonaqueous electrolyte at nonaqueous electrolyte, and 20 mass % addition of the mixture which contains an annular phosphazene compound and a chain-like phosphazene compound with the mass ratio of 80:20 further at this was done to nonaqueous electrolyte. This is made into an example 3.

[0020] 20 mass % addition of an annular phosphazene compound was done to nonaqueous electrolyte at nonaqueous electrolyte. Let this be the example 1 of a comparison. 20 mass % addition of a chain-like phosphazene compound was done to nonaqueous electrolyte at nonaqueous electrolyte. Let this be the example 2 of a comparison. 20 mass % addition of the mixture which contains an annular phosphazene compound and a chain-like phosphazene compound in nonaqueous electrolyte with the mass ratio of 80:20 was done to nonaqueous electrolyte. Let this be the example 3 of a comparison. 1 mass % addition of phosphoric ester was done to nonaqueous electrolyte at nonaqueous electrolyte, and 20 mass % addition of the mixture which contains an annular phosphazene compound and a chain-like phosphazene compound with the mass ratio of 80:20 further at this was done to nonaqueous electrolyte. Let this be the example 4 of a comparison. 1 mass % addition of N methyl acetamide was done to nonaqueous electrolyte at nonaqueous electrolyte. Let this be the example 5 of a comparison. Let the nonaqueous electrolyte which is not having the phosphazene compound and N methyl acetamide added be the example 6 of a comparison.

[0021] It is the following, and the fire retardancy of the electrolyte of the above-mentioned examples 1-3 and the examples 1-6 of a comparison was made and evaluated. It receives horizontally, as shown in drawing 1, as the principal plane becomes 45 degrees, it leans to them the test piece 1 which judged the separator which consists of porosity polyethylene which sank in these electrolytes in width of face of 12.7mm, and die length of 127mm, and was obtained, the cross direction is leveled further, and the edge of one of these is held by the stand 2. The flame of the methane gas burner 3 is hit to the other-end section from the lower part, and a test piece 1 is made to light. The combustion flame of a test piece 1 measured time amount until it reaches marked-line 4b prepared in the location of 102mm from the edge, after reaching marked-line 4a prepared in the location of 25.4mm from the lit edge.

[0022] The lithium content cobalt oxide (LiCoO₂) powder 90 mass section as positive active material, the artificial-graphite powder 5 mass section as an electric conduction agent, and the polyvinylidene fluoride 5 mass section as a binder were mixed to the N-methyl-2-pyrrolidone, and the slurry was prepared. The obtained slurry was cut out to aluminium foil, after spreading and desiccation and a foil were cut out in predetermined size, and the positive-electrode plate was obtained. The artificial-graphite 98 mass section as a negative-electrode active material, the carboxymethyl-cellulose 1 mass section as a thickener, and the styrene-butadiene-rubber 1 mass section as a binder were mixed in water, and the slurry was prepared. The obtained slurry was cut out to copper foil, after spreading and desiccation and a foil were cut out in predetermined size, and the negative-electrode plate was obtained.

[0023] It inserted in the sheathing object which consists of a resin layer which covers aluminum and its front face on both sides of the separator which consists of porosity polyethylene among both the positive-electrode plate and negative-electrode plate which were obtained as mentioned above, the further above-mentioned electrolyte was poured in there, and net volume produced the rechargeable lithium-ion battery of 600mAh(s), respectively.

[0024] The obtained cell was charged until cell voltage amounted to 4.2V in 600mA constant current, and it charged by the constant voltage of 4.2V until the charging current was set to 30mA to the pan after 4.2V attainment. The charged cell was made to discharge until cell voltage fell to 2.75V by the 600mA discharge current, and the discharge capacity of a cell was calculated. It asked for the ratio (return rate) of the discharge capacity after preservation for four days at 80 degrees C to the ratio (initial effectiveness) of the initial discharge capacity to initial charge capacity, and the discharge capacity before preservation.

[0025] The result of fire-resistant evaluation and the result of discharge characterization are shown in Table 1.

[0026]

Table 1]

	添加物 1	添加物 2	初期効率 (%)	保存復帰率 (%)	燃焼性
実施例 1	Nメチルアセトアミド 1質量%	環状ホスファゼン 20質量%	8.8	8.9	○
実施例 2	↑	鎖状ホスファゼン 20質量%	9.1	8.2	○
実施例 3	↑	環/鎖=80/20 20質量%	9.1	9.1	◎
比較例 1	なし	環状ホスファゼン 20質量%	8.8	7.7	○
比較例 2	↑	鎖状ホスファゼン 20質量%	9.1	7.5	△
比較例 3	↑	環/鎖=80/20 20質量%	9.1	7.6	△
比較例 4	リン酸エステル 1質量%	環/鎖=80/20 20質量%	8.1	7.2	○
比較例 5	Nメチルアセトアミド 1質量%	なし	9.0	7.0	△
比較例 6	なし	なし	9.0	7.0	△

[0027] In addition, the case where took fire-resistant evaluation for flame to arrive at the first reference point 20 seconds or more, and it digests among 2 reference points is made into O. The period until flame arrives at the first reference point is less than 20 seconds, and the case where the fire is extinguished among 2 reference points is made into O. By the time flame arrived at the first reference point, it required 20 seconds or more, and the case where the rate of combustion between 2 reference points was the following by 20mm/was made into **, by the time flame arrived at the first reference point, it required 20 seconds or more, and the case where the rate of combustion between 2 reference points was above by 20mm/was made into x.

[0028] As shown in Table 1, the cell of the examples 1-3 including the both sides of N methyl acetamide and a phosphazene compound is excellent in the discharge property after the first stage and preservation compared with the example of a comparison, and those electrolytes are further excellent also in fire retardancy. Especially the cell of the example 3 including the both sides of an annular phosphazene compound and a chain-like phosphazene compound shows the extremely excellent preservation property. Moreover, the electrolyte used for it shows high fire retardancy.

[0029] Next, the discharge property of a cell over the addition of a phosphazene compound in the case of including the both sides of an amide compound and a phosphazene compound and electrolytic fire retardancy are explained. 1 mass % addition of N methyl acetamide was done to nonaqueous electrolyte at nonaqueous electrolyte, and 0.05-95 mass % addition of the mixture which contains an annular phosphazene compound and a chain-like phosphazene compound with the mass ratio of 80:20 further at this was done to nonaqueous electrolyte. The fire retardancy of the obtained electrolyte is shown in Table 2. Moreover, the discharge property of the cell assembled like the above-mentioned example using them is shown in Table 2 and drawing 2.

[0030]

[Table 2]

	添加物 1	ホスファゼン 化合物	初期効率 (%)	保存復帰率 (%)	難燃性
実施例 4	Nメチルアセトアミド 1質量%	環/鎖=80/20 0.5質量%	91	82	○
実施例 5	↑	環/鎖=80/20 0.1質量%	91	82	○
実施例 6	↑	環/鎖=80/20 0.4質量%	91	82	○
実施例 7	↑	環/鎖=80/20 0.5質量%	91	86	○
実施例 8	↑	環/鎖=80/20 0.9質量%	91	87	○
実施例 9	↑	環/鎖=80/20 1質量%	91	91	○
実施例 10	↑	環/鎖=80/20 20質量%	91	92	○
実施例 11	↑	環/鎖=80/20 25質量%	91	90	○
実施例 12	↑	環/鎖=80/20 50質量%	91	90	○
実施例 13	↑	環/鎖=80/20 65質量%	90	83	○
実施例 14	↑	環/鎖=80/20 90質量%	90	82	○
実施例 15	↑	環/鎖=80/20 95質量%	83	82	○

[0031] As shown in Table 2 and drawing 2, the discharge capacity after preservation improves by adding a phosphazene compound to nonaqueous electrolyte with an amide compound irrespective of the addition. Especially, if the additions of a phosphazene compound are 0.5 to 50 mass %, especially one to 20 mass % to nonaqueous electrolyte, initial discharge capacity and the discharge capacity after elevated-temperature preservation will be improved greatly.

[0032] Next, the compounding ratio of annular phosphazene and chain-like phosphazene is explained. 20 mass % addition of the mixture which does 1 mass % addition of N methyl acetamide to nonaqueous electrolyte, and contains an annular phosphazene compound and a chain-like phosphazene compound in nonaqueous electrolyte with the mass ratio of 20:80, 40:60, 50:50, and 90:10 further at this was done to nonaqueous electrolyte, and the electrolyte of examples 16-19 was prepared. The discharge property of the cell assembled like the above-mentioned example using the fire retardancy of the electrolytic solution and them which were obtained is shown in Table 3. It combines and the discharge property of the above-mentioned example 10 which shows an annular phosphazene compound and a chain-like phosphazene compound with the mass ratio of 20:80 is shown.

[0033]

[Table 3]

	添加物 1	ホスファゼン 化合物	初期効率 (%)	保存復帰率 (%)	難燃性
実施例 16	Nメチルアセトアミド 1質量%	環/鎖=20/80 20質量%	91	90	○
実施例 17	↑	環/鎖=40/60 20質量%	91	90	○
実施例 18	↑	環/鎖=50/50 20質量%	91	92	○
実施例 19	↑	環/鎖=80/20 20質量%	91	92	○
実施例 19	↑	環/鎖=90/10 20質量%	90	89	○

[0034] Also in which compounding ratio, a good property is shown and 40 / 60 - 80/20, then the nonaqueous electrolyte cell that was more excellent in an elevated-temperature preservation property and fire-resistant both sides are especially obtained with the mass ratio of (an annular phosphazene compound / chain-like phosphazene compound) in the compounding ratio of an annular phosphazene compound and a chain-like phosphazene compound so that more clearly than Table 3.

[0035]

[Effect of the Invention] According to this invention, it excels in the discharge property after first stage and elevated-temperature preservation, and the nonaqueous electrolyte cell with high safety which cannot ignite

easily also when a sheathing can is destroyed further can be offered.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing showing the outline of the fire-resistant sex test performed in the example of this invention, and (a) is the perspective view of a testing device and (b) is a front view.

[Drawing 2] It is the property Fig. showing the relation between the addition of a phosphazene compound, and the discharge capacity of the nonaqueous electrolyte cell containing it, and (a) shows an initial property and (b) shows the property after preservation.

[Description of Notations]

1 Test Piece

2 Stand

3 Methane Gas Burner

4a, 4b Marked line

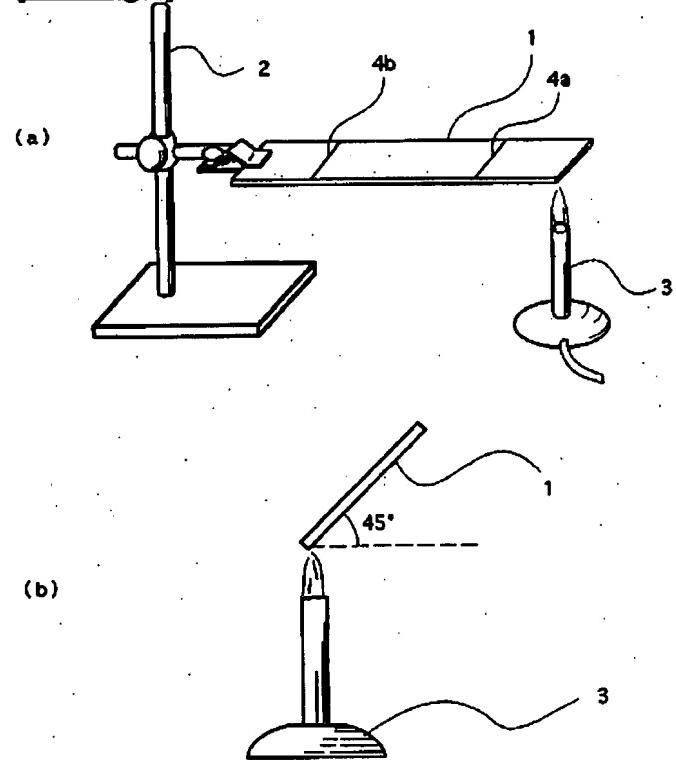
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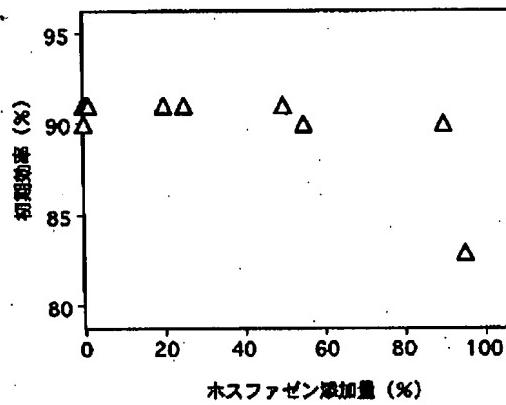
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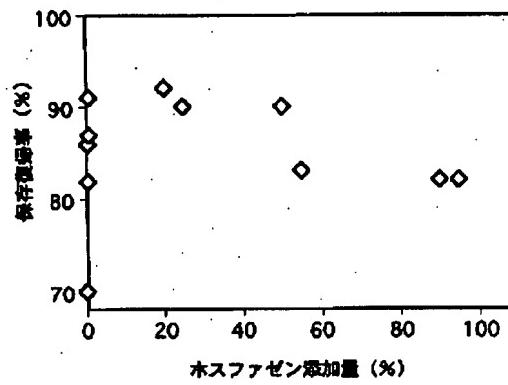
DRAWINGS

[Drawing 1]**[Drawing 2]**

(a)



(b)



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